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by

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ABSTRACT

Zirconia-toughened mullite (ZTM) ceramics were fabricated through a new experimental process, and the physical and chemical properties of these materials were determined. Significant improvements in fracture toughness and strength of the ZTM have been achieved which is attributed to the carefully controlled processing techniques.

Keywords: Tough ceramics; mullite-zirconia; zirconia toughened mullite; wear-resistant ceramic.

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CÉRAMIQUES MULLITES ENDURCIES AU ZIRCON (ZTM)

par

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RÉSUMÉ

Un nouveau procédé a été utilisé pour fabriquer des céramiques mullites endurcies au zircon (ZTM). Les propriétés physiques et chimiques de ces matériaux ont ensuite été déterminées. La ténacité à la fracture et la résistance des céramiques mullites endurcies au zircon (ZTM) ont été considérablement améliorées, ce qui semble résulter d'un meilleur contrôle des techniques de traitement.

Mots-clé : Céramiques résistantes; mullite-zircon; mullite endurci au zircon; céramiques résistant à l'usure.

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INTRODUCTION

Advanced ceramics have been under development for the past thirty years. Particularly in the past few years their application in heat engines has generated growing interest in the research and development of structural ceramics. Several advanced ceramic materials have been found suitable for engine components. They are ZrO_2 , SiC, Si_3N_4 and the sialons. Other materials such as TiB_2 and B_4C are also being examined. The advantages of using ceramics in heat engines include a greater wear resistance and better high-temperature performance than the presently known super-alloys. In addition, ceramic raw materials are more readily available than some of the strategic raw materials used in the alloys.

Among these ceramics, zirconia possesses excellent fracture toughness, but the temperature dependency of this toughness limits its uses to below $1000^\circ C$. Both SiC and Si_3N_4 provide high strength but are prone to oxidation at high temperatures. Composite materials containing whiskers, fibers or platelets in either a metal or ceramic matrix comprise another type of material considered for structural applications. Substantial improvements in strength, toughness and stiffness can be obtained in zirconia by the addition of SiC whiskers to form a composite. A major drawback of SiC whisker-reinforced materials is the high initial cost of the SiC whiskers, (approximately \$1,000 US/Kg), thus limiting their commercial exploitation.

Mullite is considered a candidate for structural ceramic applications because of its high-melting point, high thermal-shock resistance, high-temperature stability, ease of processing and low cost. Reinforcement of mullite with a second phase such as ZrO_2 could improve its mechanical properties significantly. In Japan high strength zirconia-mullite composites are under development. Mullite containing 10 vol% of zirconia and having a bend strength of 500 MPa has been reported by the Toyo Soda Mfg. Co. (1). In view of the considerable advances being made in ceramic processing, further improvements in the mechanical properties of mullite are anticipated. As a part of a project to develop the technology for the

preparation and characterization of advanced materials, a preliminary study of zirconia-toughened mullite (ZTM) ceramics was conducted at CANMET; this report summarizes the results of the study.

History of Mullite Ceramics

The mineral mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), was named after the Island of Mull in Scotland where it is found in xenoliths occurring in volcanic rocks (2). Its occurrence is rare in nature, and is most commonly found in refractory products consisting of silica and alumina. A list of the general physical and mineralogical properties of mullite is given in Table 1 (3). Mullite was first synthesized in the late 1950's as a replacement for sillimanite in refractory production due to the scarcity of the latter material. Commercially, mullite is produced by mixing fireclay and "Bayer process" alumina. The alumina content in the clay-alumina mixtures is adjusted to about 70%. The mixture is then pelletized and sintered at 1800°C to produce mullite (3). Mullites can also be produced by electrically melting the same raw materials. Mullites synthesized by the above processes contain impurities and develop heterogeneous microstructure containing a mixture of crystals and a glassy phase. The low toughness and volume instability at high temperature of mullites are attributed to this inferior microstructure (4).

In recent years, a significant amount of work has been conducted in mullite synthesis. Efforts to improve the physical and chemical characteristics of the material have focussed on sol-gel and wet-chemical processing of the raw materials. Table 2 shows the chemical characteristics of the mullites synthesized by various techniques (3). It can be seen from the table that improved chemical properties of mullites are obtained by improved processing techniques.

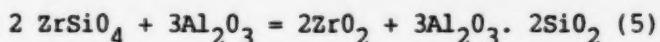
High-purity mullites are being developed under a cooperative program between the Industrial Research Institute and business firms in Japan. They produced various types of mullites including transparent mullite, mullite of

99.9% purity and with a bend strength of 400 MPa at 1400°C. The cost of these mullite ceramics is estimated to be about half that of SiC and Si₃N₄ (1).

To improve the fracture toughness of mullite, zirconia is incorporated into it to form mullite-zirconia composite similar to the successfully commercialized zirconia-toughened alumina ceramics (ZTA). The mechanism of toughening of mullite by zirconia is not fully understood in contrast with the well developed mechanisms for zirconia-toughened alumina ceramics (ZTA). Therefore further research and development work on this material is necessary to make it commercially viable.

In general, zirconia-toughened mullite ceramics have been produced by the common techniques of using oxides and silicates as starting materials. The mixtures were then formed by pressing and then densified by sintering at high temperature. In order to produce highly dense ZTM ceramics, closely controlled processes are necessary. The two common processing techniques are:

- (a) sintering the mixture containing mullite and zirconia; and
- (b) sintering the mixture containing zircon and alumina to form zirconia and mullite according to the following reaction:



In order to obtain desirable physical properties, great care must be exercised in the preparation of the powder from the starting raw materials. Inferior properties are attributed to the development of inhomogeneous microstructures caused by voids, phase separation, non-uniform particle size and impurities. The ideal starting powders should be free from impurities and agglomerates and should have a grain size less than 2.0 μm (6).

By using sol-gel or wet-chemical processes, high purity, highly reactive, superfine and uniform powders can be readily obtained. This avoids the problems encountered in the conventional ceramic powder preparation techniques involving grinding and mixing of oxides and silicates.

Other factors known to affect the physical properties of the material are the forming and sintering of the green bodies. The final sintered density of the ceramics is influenced by the initial green density of the material and this has been demonstrated by Bruch in his study in the sintering kinetics of dense alumina (7). The formation of voids in sintering has been discussed in detail by Coble (8). To control or restrict the formation of the pores, dense packing of the green bodies is necessary. This may be accomplished by using isostatic pressing. Normally the ZTM bodies are sintered at about 1600°C; the heating rate and soak-time can critically affect the final properties of the products.

EXPERIMENTAL

Materials: The starting powders used for this study were obtained from commercial sources. The high purity synthetic mullite powder was purchased from Bakowski and the unstabilized monoclinic zirconia powder was detained by the Harshaw Company. Reagent grade MgO was used as a stabilizing agent. Laboratory-prepared freeze-dried mullite,(9) calcined to 1000°C overnight was also used to replace the commercially available mullite.

Procedure: A mixture containing 85 vol% mullite, 15 vol% unstabilized zirconia and the required amount of stabilizing agent (MgO) was prepared. Homogeneous mixing and grain size reduction were achieved by attrition-mill with zirconia balls in water for 2 hours. The resulting slurry was then dried in a Flash-Evaporator* and the powders were characterized by surface area. Discs of 37 mm diameter by 3 mm thick were obtained by uniaxially pressing the dried powder with drops of PVA binder solution in a steel die at 150 to 200 MPa. After drying at 100°C and oxidizing the organic binder at 700°C, these discs were fired in air at 1640°C for 1 hr.

*Buchler Instruments, Fort Lee, N.J., U.S.A.

The amount of tetragonal zirconia in the sintered mullite-zirconia discs was measured by an XRD technique using the following equation (10):

$$\%t\text{-ZrO}_2 = [I_a(t)/(I_b(m) + I_c(m) + I_a(t))] \times 100$$

$I_a(t)$ = intensity of $d = 0.2949$ nm peak for tetragonal zirconia,

$I_b(m)$ = intensity of $d = 0.316$ nm peak for monoclinic zirconia, and

$I_c(m)$ = intensity of $d = 0.2834$ nm peak for monoclinic zirconia

The mechanical strength and Young's modulus of the ZTM samples were measured on an Instron mechanical tester with the aid of a grid using three point circle geometry. The following equations were used for the calculation:

For flexural strength (11):

$$f = L[(1+v) \{0.485 \log(R/h) + 0.52\} + 0.48]/h^2$$

where f = flexural strength

L = maximum load applied on specimen

v = Poisson's ratio (0.26)

R = radius (1.27 cm) and

h = thickness

For Young's modulus (11):

$$E = 0.754 LR^2/h^3$$

where E = Young's modulus,

W = displacement at the centre of the disc,

L = load

R = radius and

h = thickness

Both hardness and fracture toughness were measured using a Tukon hardness tester. A schematic of crack geometry is shown in Fig. 1 and the following equations were used for calculations.

For hardness (12):

$$H = 0.47P/a^2$$

where H = hardness

P = fixed weight (10 kg) on indentation and

a = half of diagonal of indentation

For fracture toughness (13):

$$K_{IC} = 0.031 (E/H)^{0.4} (L/C^{1.5})$$

K_{IC} = toughness

C = half of the crack length

The microstructure and elemental distributions in the specimens were determined by scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Characterization of Powders and Green Discs

The milled powder used for sample preparation had a specific surface area of $>30\text{m}^2/\text{g}$ as measured by BET. During the forming stage, minor laminations were observed in some of the specimens and this problem was resolved by adjusting the moisture content in the powders. The specimen which cracked due to laminations were pulverized and repressed. This repressing technique increased the green density (Table 3).

Effect of Sintering Temperatures on the Physical Characteristics of ZTM

The optimum sintering temperature at a constant sintering time of 1 hour was established from measurement of the water absorption of the product given in Table 4. It can be seen that the minimum water absorption was obtained in specimens fired at 1640°C .

After sintering, most samples were slightly translucent without any cracks, and had a smooth surface texture. Some samples showed a very small crack located in the centre of the disc. These cracked specimens had been pressed twice when forming (i.e. pulverized and repressed) and the crack was apparently caused by non-uniform packing of agglomerated particles from pulverization.

The densities of these samples are given in Table 5. A density of 99.8% was obtained from samples containing commercial mullite and about 95% from samples containing freeze-dried mullite. The lower density obtained from samples containing freeze-dried mullite is probably attributed to the poorly crystallized mullite formed at a relatively low calcination temperature of 1000°C .

It appears that the characteristics of the starting powders were critical for obtaining the desirable properties of the final products.

Many defects in the fabricated ceramics are due to inhomogeneities in micro-structures such as voids, grain size variations and contaminations. The non-uniformity and agglomeration of powders in the starting materials often cause micro-voids and micro-cracks in the texture of final products. The poor reactivity of starting powders also causes pores at grain boundaries.

Another aspect of the results in this study was that there is a correlation between the green densities and the relative densities on firing. To obtain theoretical density for the final products it was necessary to achieve a high-packing density at the forming stage of the discs.

Microstructure of the Sintered ZTM

The microstructures of the ZTM were examined by the SEM technique. The result shown in Fig. 2 indicates that the zirconia blebs of about $1.0\ \mu\text{m}$ in size are dispersed uniformly in the mullite matrix. At higher magnification, the microstructure shows that the zirconia blebs are irregularly shaped (Fig. 3A). EDXR maps for Mg, Si, Al and Zr, given in Fig. 3 B-E, indicate that most of the stabilizing agent (MgO) is dispersed in the mullite matrix. The relatively low MgO content in the ZrO_2 phase indicates that most of the MgO has reacted with Si and/or Al from the mullite to form a magnesium spinel phase or a glassy phase composed mainly of Magnesium alumino silicates.

Tetragonal Zirconia Content of ZTM

In this investigation 9 mole % MgO was added to the zirconia contained in the mixture. The surface of the resulting sintered partially-stabilized, zirconia-mullite discs was examined by XRD using a diffractometer. The diffraction peak intensities of the (111) for tetragonal, and (111) and (111) for monoclinic zirconia were obtained from

the charts, and the % tetragonal zirconia in the mullite matrix was estimated. (Typical diffractometer traces of the ZTM samples are given in Fig. 4). The calculated tetragonal phase content in the as-sintered discs was 34%. For the polished sintered discs, the tetragonal phase content dropped to 23% indicating that some of the tetragonal phase reverted back to monoclinic on mechanical polishing. From EDXR and XRD results it was suspected that ZrO_2 had not been stabilized by MgO but pure ZrO_2 had been encased in a hard matrix of mullite on firing and this encasing had prevented the high-temperature tetragonal phase of ZrO_2 from reverting back to monoclinic form at room temperature.

Mechanical Properties of ZTM

The measured flexural strength, toughness and other mechanical properties of the ZTM in this work are given in Table 6. Also included in the Table are data from literature sources on zirconia-mullite materials fabricated by similar processes. The pure mullite material is also included in the Table for comparison. Of these, the highest values are established by the material produced in the present investigation. Further improvements of the mechanical properties on the ZTM may be possible by improving the raw materials and developing better forming techniques. The optimization of the zirconia mullite ratio may also improve the mechanical properties.

As mentioned previously, zirconia-toughened mullite can be fabricated from the high-temperature reaction of zircon-alumina mixtures. Presently, there are several active investigations elsewhere into these reaction-sintered materials (15,17,18). The literature data for these reaction-sintered zircon-alumina ceramics suggest they exhibit higher flexural strength at room temperature than zirconia-mullite materials. This is apparently due to the glassy phases produced by the decomposition of zircon. Although the zircon and alumina raw materials are inexpensive, the difficulty of eliminating the glassy phases from the mixtures may limit their use at high temperatures.

CONCLUSIONS

It has been shown that the incorporation of MgO stabilized zirconia in a sintered mullite composite results in an increase in both the M.O.R. and fracture toughness of the matrix. In the case of 15 vol % monoclinic-ZrO₂ and MgO stabilizer added to mullite and sintered to full density at 1640°C, the M.O.R. increases to over 300 MPa for the zirconia-mullite composite compared with the original value of 150 MPa for ZrO₂-free mullite. Similarly, the fracture toughness K_{Ic} increases from 1.8 to 4.5 MPa m^{1/2} with the addition of zirconia.

These mechanical properties of the materials developed so far are superior to those reported in the literature. As no major change in overall processing and capital equipment is required to achieve these improvements, and as raw material costs are increased less than 25%, it is anticipated that this material will have applications in many wear-resistant and impact-resistant uses. Further studies to optimize the processing in order to maximize the M.O.R. and fracture toughness in particular are underway.

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Table 1: Physical and Mineralogical Properties of Mullite

Chemical formula	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$
Crystal system	Orthorhombic
a	0.749 nm
b	0.763 nm
c	0.287 nm
Specific gravity	3.03–3.16 g/cc (measured) 3.170 (calculated)
Hardness (Mohs')	6 – 7
Melting point	1810°C
Al_2O_3	71.8%
SiO_2	28.2%

Table 2: Chemical Compositions of Mullites from Various Sources

	Calcined mullite	Fused mullite	Sol-Gel processed
SiO ₂	25.23%	25.36%	28.2%
Al ₂ O ₃	72.34%	73.41%	71.8%
Fe ₂ O ₃	0.62%	0.17%	0.008%
TiO ₂	0.12%	0.05%	0.005%
CaO	0.19%	0.27%	-
MgO	0.25%	0.15%	0.005%
Na ₂ O	0.42%	0.34%	0.009%
K ₂ O	0.42%	0.15%	-
L.O.L.	0.19%	-	-
Minerals	mullite corundum glass	mullite glass	mullite > 99.9%

Table 3: The Effect of Repressing on the Green Density of Mullite-ZrO₂ Mix

	1	2	3	4	5	6	7
Forming pressure (MPa)	150	150	150	200	200	150	200
Pressed	once	once	twice	twice	twice	twice	once
Dry-density (g/cc)	1.43	1.43	1.61	1.55	1.66	1.91	1.90
Particulars	<—————> Freeze-dried mullite and Zirconia mix					<—————> Commercial mullite & Zirconia mix	

Table 4: The Effect of Firing Temperatures on the Water Absorption of Mullite-ZrO₂ Specimens

Firing Temp.	Water absorption on freeze-dried mullite and ZrO ₂ mixture	Water absorptions on commercial mullite & ZrO ₂ mix
1600°C	1.67%	0.18%
1630°C	1.41%	0.11%
1640°C	1.29%	0.06%
Melting point	1710°C	1700°C

Table 5: The Densities of the Specimens

	1	2	3	4	5	6	7
Dry-density (g/cc)	1.43	1.43	1.61	1.55	1.66	1.91	1.90
Fired-bulk density (g/cc)	3.35	3.33	3.34	3.29	3.27	3.41	3.39
Relative density* (%)	94.3	94.3	96.3	95.9	95.8	99.8	99.8
Particulars	$\longleftrightarrow$ Freeze-dried mullite & ZrO_2 mix.					$\longleftrightarrow$ Commercial mullite & ZrO_2 mix.	

* Relative density = Fired bulk density/True density

(The fired bulk density was determined by the mass and dimensional measurements and the true density was measured by a liquid displacement.)

Table 6: A Comparison of Mechanical Properties of ZrO_2 -Toughened Mullite Ceramics

No.	1	2	3	4	5	6
Raw materials	$\longleftrightarrow$ mullite and ZrO_2			$\longleftrightarrow$ mullite		
Flexural strength (MPa)	302	—	200	290	120	150
Young's modulus (GPa)	337	170	ND	ND	190	ND
Toughness K_{Ic} (MPa $m^{1/2}$)	4.5	2.5	3.5	3.1	2.5	1.8
Hardness (GPa)	10	—	ND	ND	ND	ND
References	This work	(14)	(15)	(15)	(16)	(15)

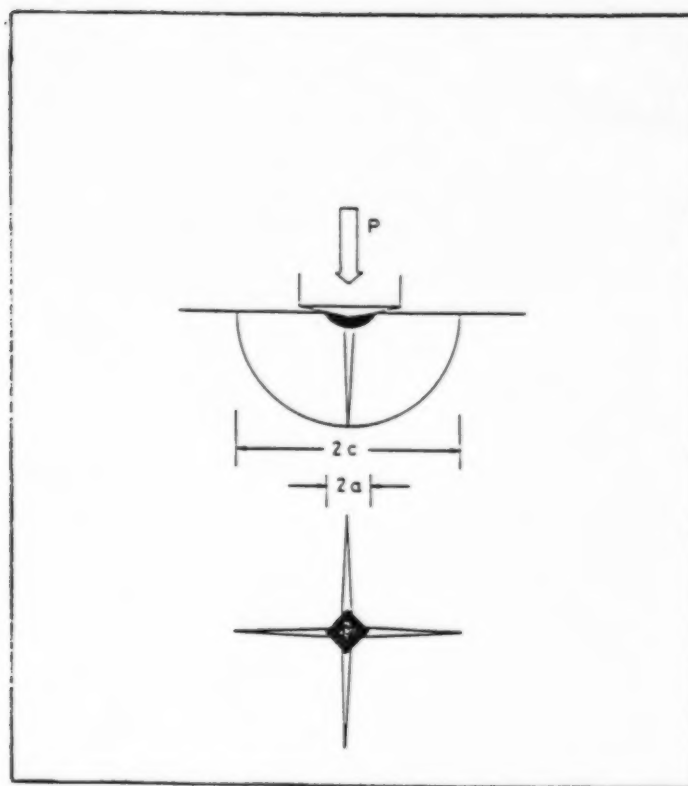


Fig. 1 Schematic of Crack Geometry on Tukon Hardness Tester

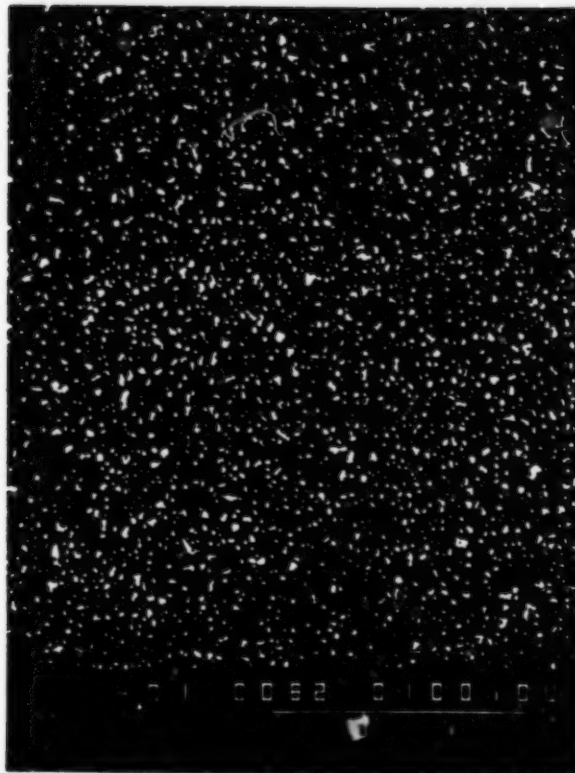


Fig. 2. SEM Micrograph Showing the Distribution of Zirconia Particles

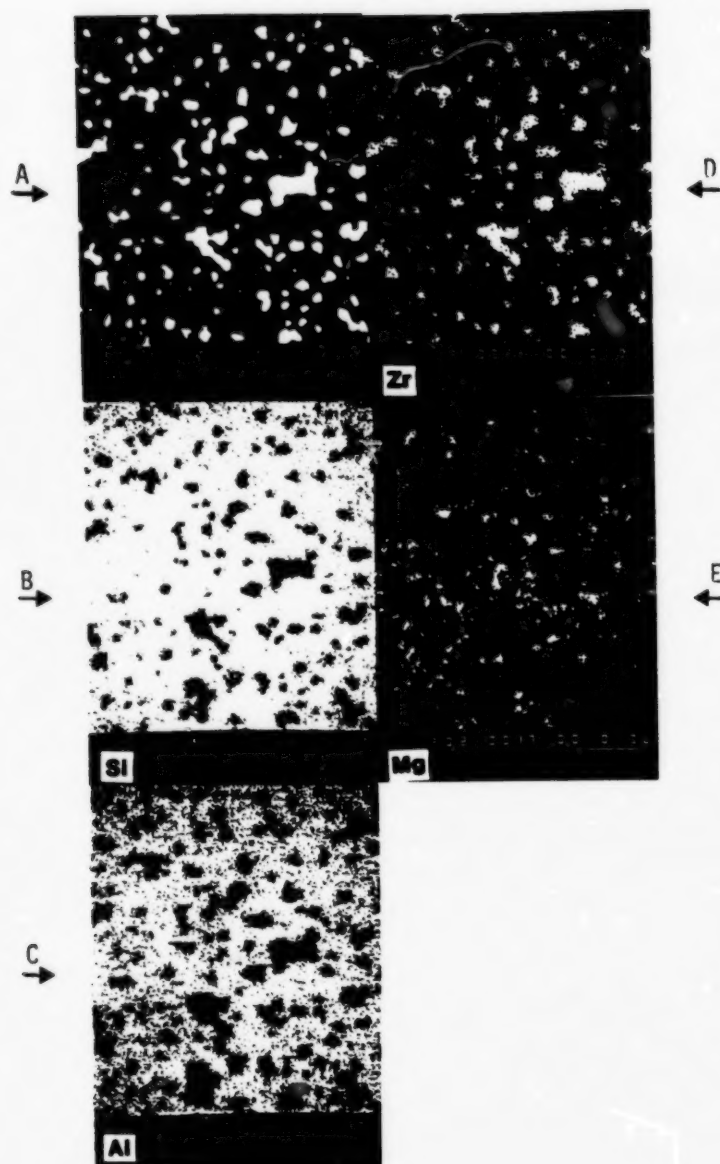


Fig. 3. SEM Micrograph (A) and EDXR Maps (B-E) of Sintered Specimen

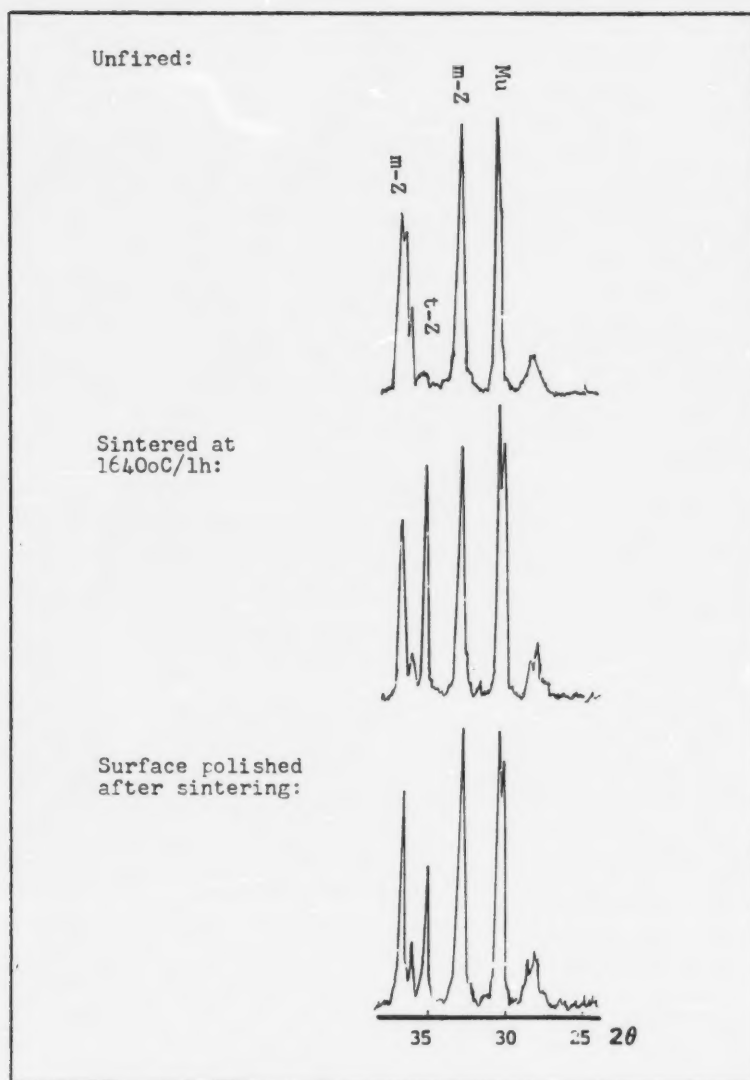


Fig. 4. Diffractometer Traces of Specimens. Mu:mullite, m-Z:m-Zirconia, t-Z:t-zirconia